1- Carboxylic esters

Nomenclature

The functional group of a carboxylic ester is an acyl group bonded to OR or OAr, where R represents an alkyl group and Ar represents an aryl group. Both IUPAC and common names of esters are derived from the names of the parent carboxylic acids. The alkyl or aryl group bonded to oxygen is named first, followed by the name of the acid in which the suffix -ic acid is replaced by -ate.

Synthesis

Many carboxylic esters are made by Fischer esterification; that is, by heating a mixture of the carboxylic acid and alcohol together with a strong acid (often sulfuric) as a catalyst. It has been established that, in this reaction, the OR oxygen atom of the ester in most cases comes from the alcohol and not from the carboxylic acid. This evidence was provided through isotopic-labeling experiments, in which the oxygen atom of the alcohol used was oxygen-18 (^{18}O). In the product of the esterification, the ^{18}O remained with the R group of the alcohol.

$CH_3COOH + C_2H_5OH + H_2SO_4$ ----- $CH_3COOC_2H_5 + H_2O$

Or from acetyl chloride and ethyl alco.

$CH_3COCl + C_2H_5OH$ --------- $CH_3COOC_2H_5 + HCl$

Because the molecules of a carboxylic ester cannot form hydrogen bonds with one another (as both carboxylic acids and alcohols do), the boiling point of an ester RCOOR′ is usually lower than that of the corresponding acid RCOOH, especially when R′ is a methyl or ethyl group. For example, the boiling point of acetic acid (CH_3COOH) is 118 °C (244 °F), while that of ethyl acetate ($CH_3COOCH_2CH_3$) is 77 °C (171 °F).

Reactions

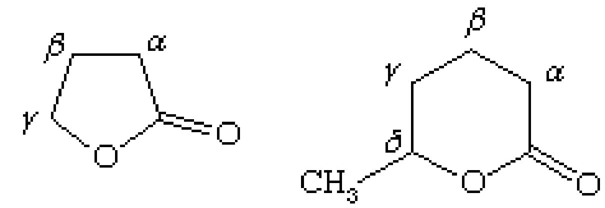
The most important reaction of carboxylic esters is hydrolysis under basic conditions.

$$\underset{\text{carboxylic ester}}{RCOOR'} + H_2O \xrightarrow{OH^-} \underset{\text{carboxylate ion}}{RCOO^-} + \underset{\text{alcohol}}{R'OH}$$

Esters can also be hydrolyzed under acidic conditions, but hydrolysis under basic conditions is generally preferred because it is not reversible. The base hydrolysis is called saponification, because soap (Latin: *sapo*) has always been manufactured by heating fats (which are carboxylic esters) with water and a basic substance (originally wood ash).

Lactones

Cyclic esters are called lactones. In these cases the COOH and OH groups that combine to form water are part of the same molecule .

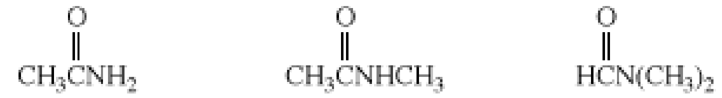


γ-butyrolactone (from butyric acid)   δ-caprolactone (from caproic acid)

Amides

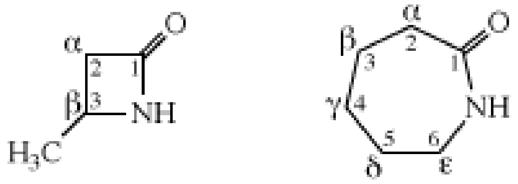
Nomenclature

The functional group of an amide is an acyl group bonded to a trivalent nitrogen atom. Amides are named by dropping the suffix -oic acid from the IUPAC name of the parent acid, or -ic acid from its common name, and replacing it by -amide. If the nitrogen atom of an amide is bonded to an alkyl or aryl group, the group is named and its location on nitrogen is indicated by N-. Two alkyl or aryl groups on nitrogen are indicated by N,N-di. Amide bonds are the key structural feature that joins amino acids together to form polypeptides and proteins.



acetamide (a 1° amide) | N-methylacetamide (a 2° amide) | N,N-dimethyl formamide (a 3° amide)

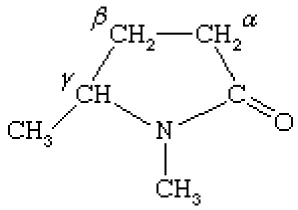
Cyclic amides are called lactams. Their common names are derived in a manner similar to those of lactones, with the difference that the suffix -olactone is replaced by -olactam. Caprolactam is the starting material for the synthesis of nylon-6.



3-butanolactam (β-butyrolactam) | 6-hexanolactam (ε-caprolactam)

Penicillins—the most effective antibiotics of all time—are a family of compounds, all of which have in common a four-membered β-lactam ring fused to a five-membered thiazolidine ring. The penicillins owe their antibiotic activity to a common mechanism that inhibits the synthesis of a vital part of bacterial cell walls.

The cephalosporins, another class of β-lactam antibiotics, have an even broader spectrum of antibiotic activity than the penicillins and are effective against many penicillin-resistant bacterial strains.



N-methyl-γ-valerolactam
(from valeric acid)

Synthesis

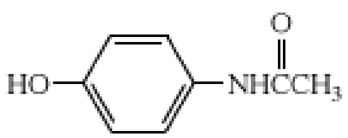
The only important practical method for preparing amides is to treat an acyl chloride or anhydride with ammonia or a primary (RNH_2) or secondary (R_2NH) amine. Two moles of ammonia or amine are required—one to form the amide and one to neutralize the HCl or carboxylic acid by-product.

$$CH_3COCl \quad + \quad NH_3 \quad \text{--------} \quad CH_3COMH_2 \quad + HCl$$

$$CH_3COOCOCH_3 \; + \; NH_3 \quad \text{------} \quad 2\ CH_3CONH_2$$

Properties

With the exceptions of formamide ($HCONH_2$) and some of its *N*-substituted derivatives, all amides are solids at room temperature. They are neutral compounds, neither acidic nor basic. An amide called acetaminophen (*N*-*para*-hydroxy-phenylacetamide) is a pain reliever sold without prescription under several different proprietary names, one of which is Tylenol.



acetaminophen

Reactions

Like all other acid derivatives, amides can be hydrolyzed to yield carboxylic acids (under acidic conditions) or the salts of carboxylic acids (under basic conditions), but, because amides are less reactive, these reactions require more strenuous conditions than hydrolysis of the other derivatives.

CH_3CONH_2 + HCl ------- CH_3COOH + NH_4OH
CH_3CONH_2 + NaOH ------ CH_3COONa + NH_3

Amides without substituents on the nitrogen can be dehydrated to nitriles with many dehydrating agents, of which phosphorus pentoxide (P_4O_{10}) is the most common.

$$RCONH_2 \rightarrow RC\equiv N + H_2O$$

The nylons are a family of polymers, the members of which have subtly different properties that suit them to one use or another. The two most widely used members of this family are nylon-6,6 and nylon-6. Nylon-6, so named because it is synthesized from caprolactam, a six-carbon monomer, is fabricated into fibres, brush bristles, rope, high-impact moldings, and tire cords.